Response to Comment by Zeebe and Tyrrell on “The Effects of Secular Calcium and Magnesium Concentration Changes on the Thermodynamics of Seawater Acid/Base Chemistry: Implications for the Eocene and Cretaceous Ocean Carbon Chemistry and Buffering”

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We thank Zeebe and Tyrrell (hereafter Z&T) for their insightful analysis of the bicarbonate-to-carbonic acid stoichiometric equilibrium constant \(K_1^*\) calculated using the MyAMI model in our original study (hereafter H15), which is indeed “perplexing,” as they put it, given conventional wisdom (e.g., Garrels & Thompson, 1962) regarding the importance of complex formation between divalent cations and bicarbonate. Upon re-evaluation of the specific ion interaction coefficients of our Pitzer-type model, we identified as suspect the calcium-bicarbonate coefficients \(f_{Ca-HCO_3}^{(0)}\) of Harvie et al. (1984; \(f_{Ca-HCO_3}^{(0)} = 0.4\) and \(f_{Ca-HCO_3}^{(1)} = 2.977\); see their Table 1) and replaced them with values taken from He and Morse (1993; \(f_{Ca-HCO_3}^{(0)} = 0.2\) and \(f_{Ca-HCO_3}^{(1)} = 0.3\); see their Table 5) to resolve the discrepancy regarding \(K_1^*\) predicted by our MyAMI model and the measurements of \(K_1^*\) in the NaCl-MgCl2-CaCl2 system by Pytkowicz and Hawley (1974) cited by Z&T (see top row in Figure 1). We note that for the comparison of MyAMI results against the Pytkowicz and Hawley (1974) experimental data, it is necessary to exactly replicate their brine compositions (including sodium and chloride changes) and make the same assumption for the activity coefficient of aqueous CO2 (\(γ_{CO_2} = 1.178\); see Pytkowicz & Hawley, 1974, Table 2 and equations 5 and 6).

Further, as pointed out in the comment by Z&T, the bicarbonate activity coefficient (\(γ_{HCO_3}\)) that is affected by \(f_{Ca-HCO_3}^{(0)}\) enters into the calculation of both the bicarbonate-to-carbonate ion stoichiometric equilibrium constant \(K_2^*\) as well as \(K_1^*\). However, \(γ_{HCO_3}\) cancels in the product of \(K_1^*\) and \(K_2^*\), which was also experimentally determined by Pytkowicz and Hawley (1974). These additional data thus offer a powerful test of the skill of our MyAMI model to correctly predict the carbonate ion activity coefficient (\(γ_{CO_3}\)), which is very strongly affected by complex formation between divalent cations and carbonate ion (e.g., Garrels & Thompson, 1962; Pytkowicz & Hawley, 1974) and thereby is the dominant cause of the calcium and magnesium dependence of \(K_2^*\), \(K_1^*\), \(K_{Ca}^*\), and the CaCO3 saturation product \(K_{sat}^*\). We find excellent agreement between measured and MyAMI-predicted \(K_1^*\) and \(K_2^*\), regardless of the choice of \(f_{Ca-HCO_3}^{(0)}\) (bottom row Figure 1). This outcome is further evidence of the skill of the Pitzer-type specific ion interaction modeling approach employed by H15 in producing accurate equilibrium constants in solutions of high ionic strength.

It is important to point out that using the suspect Harvie et al. (1984) \(f_{Ca-HCO_3}^{(0)}\) parameters has minimal implications for the main conclusions reached in our original study. The \(Ω-pH-CO_2\) relationship is not affected by the choice of \(f_{Ca-HCO_3}^{(0)}\) because it depends on the product of \(K_1^*\) and \(K_2^*\), such that the affected bicarbonate activity coefficient \(γ_{HCO_3}\) cancels out (i.e., Figure 1 bottom row; see H15 equation 2 where the product appears in logarithmic notation as the sum of \(pK_1^*\) and \(pK_2^*\)). The error does affect the total carbon concentration, declining colored contours (DIC), inferred for a given \(Ω-pH-CO_2\) state (H15 equation 3), but the resulting DIC error is of order of only a few percent (Figure 2), too small to change the conclusions of H15. To stress this point, we highlight two passages from the original study: (a) “[...] the strong effect of changes in divalent cation concentration [mainly via \(γ_{CO_3}\)] essentially cancels in the aggregate pK* terms, such that the relationships between DIC, pH, Ω, and CO2 are approximately constant [...]”; and (b) seawater buffering and “[...] the sensitivity to incremental DIC and ALK change is very closely tied to [H+] while being essentially insensitive to DIC [...]. The concentration of [Ca2+]", however, is a direct factor in the calculations of CaCO3 saturation, and thus, it appears as a separate term in the relationships among DIC, pH, Ω, and CO2 (equations (2) and (3) in H15).” That is, while regrettable, the few percent error in bicarbonate activity coefficient is simply too small...
to significantly impact the results of H15, which are fundamentally driven by the doubling and quadrupling of seawater calcium concentration in the CaCO$_3$ solubility product, not the effects of magnesium and calcium change on the equilibrium constants, when going back to Eocene and Cretaceous times, respectively.

The initial motivation for developing MyAMI was the known inaccuracy of the previously published correction factors for $K_1^*$, $K_2^*$, and $K_{sp}^*$ (i.e., Ben-Yaakov & Goldhaber, 1973; Tyrrell & Zeebe, 2004). Ben-Yaakov and Goldhaber (1973) extrapolate from the seminal work by Garrels and Thompson (1962), who first systematically described the importance and implications of "ion pairing" (i.e., complex formation) for seawater carbonate chemistry and speciation. Based on very limited empirical data, Garrels and Thompson gave rise to the conventional wisdom, which Z&T call upon, that most of carbonate ion and much of bicarbonate ion is complexed to divalent cations. Ben-Yaakov and Goldhaber translated these foundational results into inferred dependences of conditional equilibrium constants $K_1^*$ and $K_2^*$ and $K_{sp}^*$. However, it has since been shown (e.g., Pytkowicz & Hawley, 1974) that complexation of bicarbonate ion is much less prevalent in seawater than originally envisioned by Garrels and Thompson (1962). As for the Tyrrell and Zeebe (2004) correction factor for the CaCO$_3$ solubility product $K_{sp}^*$, it was already pointed out by Roberts and Tripati (2009) that the derivation
of their formulation is based on the inappropriate extrapolation of experimental data. Tyrrell and Zeebe (2004) fit a magnesium-to-calcium ratio dependence. In this response we show that MyAMI yields $K_1$ and $K_2$ with absolute values consistent with the Pytkowicz and Hawley (1974) experimental results, after changing the code to correct the suspect $\beta(0,1)$ Ca-HCO₃ and appropriately accounting for the vast changes in NaCl concentration in the Pytkowicz and Hawley (1974) data set. MyAMI also appropriately reproduces the empirically determined equilibrium constants for modern seawater composition temperatures of 0 to 30°C and salinities of 30 to 40 (see Figure 3 in H15). This demonstrates the skill of the Pitzer model approach MyAMI is based on to calculate equilibrium constants for seawater and nonseawater brines. We are unaware of any similarly rigorous testing of the Ben-Yaakov and Goldhaber (1973) and Tyrrell and Zeebe (2004) correction factors, which we argue should not be used anymore.

Z&T close their comment with the notion that “[…] future research efforts should include experimental determination of stoichiometric equilibrium constants […] for the particular major ion compositions of past oceans […]” We would like to point out that experimental determination of stoichiometric equilibrium constants is an integral part in the determination of the Pitzer-type ionic interaction model parameters of the carbonate system (e.g., He & Morse, 1993) and that the utility of a well-constrained Pitzer-type model, such as MIAMI (Millero & Pierrot, 1998) and MyAMI [H15], far exceeds the approach suggested by Z&T. First, past ocean major ion composition is notoriously uncertain, and propagating that uncertainty is hindered by equilibrium constants determined for a singular presumed ocean major ion composition at one particular time in Earth history. Second, geochemical work performed in artificial seawater of arbitrary composition requires equilibrium constants different to those applicable to past oceans. Third, culturing work with organisms capable of manipulating their internal major ion composition require continuous recalculation of the equilibrium constants as the major ion composition evolves. Fourth, reactions with sediments and rocks can significantly alter the composition of seawater, with implications for equilibrium constants largely unrelated to past ocean seawater. All these cases can be served with a single well-constrained Pitzer-type model of seawater, such as

![Figure 2. Comparison of the solutions of the carbonate chemistry system based on equilibrium constants derived from the MyAMI model using the suspect calcium-to-bicarbonate interaction coefficients ($\beta_{Ca-HCO_3}$) of Harvie et al. (1984; top row; identical to Figure 4 in H15) and using the alternate calcium-to-bicarbonate interaction coefficients of He and Morse (1993; bottom row). The effect of $\beta_{Ca-HCO_3}$ on the activity coefficient of bicarbonate ($\gamma_{HCO_3}$) cancels out in the relationship between pH, saturation state $\Omega$, and $CO_2$ (i.e., x and y axes and rising contours). The effect of $\beta_{Ca-HCO_3}$ on total dissolved carbon concentration (declining colored contours) is minimal, thereby not significantly affecting the conclusions of H15.](image-url)
MIAMI and MyAMI. Thus, instead of presuming the composition of past seawater from uncertain reconstructions and expending significant resources in experimentally determining the appropriate equilibrium constants (including their temperature and salinity dependencies) it seems far more fruitful to further improve the Pitzer-type models, which are indeed “seemingly convoluted” [Z&T] but also follow accepted state-of-the-art practices in physical chemistry. These comments aside, by identifying a clear parameter error in our original study, Z&T have helped to improve MyAMI.

References


